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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : G03F 7/027, G03C 9/08 C08G 59/18, 59/68	A1	(11) International Publication Number: WO 92/20014 (43) International Publication Date: 12 November 1992 (12.11.92)
(21) International Application Number: PCT/US92/03168 (22) International Filing Date: 15 April 1992 (15.04.92) (30) Priority data: 693,890 1 May 1991 (01.05.91) US 855,392 26 March 1992 (26.03.92) US (71) Applicant: ALLIED-SIGNAL INC. [US/US]; Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US). (72) Inventors: LAPIN, Stephen, Craig ; 26478 N.E. Lakeshore Drive, Wauconda, IL 60084 (US). SNYDER, James, Ronald ; 908 W. Belmont, 3rd Floor, Chicago, IL 60657 (US). SITZMANN, Eugene, Valentine ; 451 Galleon Way, Des Plaines, IL 60016 (US). BARNES, Darryl, Keith ; 4925 Twining Avenue, Bellwood, IL 60104 (US). GREEN, George, David ; 2741 Mayfield Drive, Park Ridge, IL 60068 (US).		(74) Agent: ROONEY, Gerard. P.; Allied-Signal Inc., Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US). (81) Designated States: CA, CH, DE, ES, GB, JP, NL, SE. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: STEREOLITHOGRAPHY USING VINYL ETHER-EPOXIDE POLYMERS (57) Abstract Polymer precursor formulations suitable for stereolithography may be prepared from compositions containing vinyl ether functionalized compounds and epoxy functionalized compounds plus an effective amount of a cationic photoinitiator.		

Claims

1. A polymer precursor composition for stereolithography consisting essentially of

- 5 (a) vinyl ether functionalized compounds;
(b) epoxy functionalized compounds;
(c) an effective amount of a cationic photoinitiator;

said vinyl ether compounds and epoxy compounds both being curable by acids released by said photoinitiator and having proportions selected to provide a polymeric structure having suitable green strength with
10 minimal distortion when said composition is polymerized by a light source selected from the group consisting of UV and visible light lasers.

2. A polymer precursor composition of Claim 1 wherein the proportions of said vinyl ether compounds and epoxides are defined by the formula $M = \frac{F}{E}$

15 where M is the vinyl ether equivalent weight of the composition
F is the total weight in grams of the
composition

E is the number of vinyl ether equivalents in the composition

3. A polymer precursor composition of Claim 2 wherein M is
20 between 80 and 800.

4. A polymer precursor composition of Claim 1 wherein said vinyl ether compounds are derived from at least one member of the groups consisting of urethanes, phenols, esters, ethers, siloxanes, carbonates, and aliphatic or aromatic hydrocarbons.

25 5. A polymer precursor composition of Claim 1 wherein said epoxy compounds are derived from at least one member of the group consisting of phenols, novolacs, aliphatic or cycloaliphatic polyols, and polyether polyols, and siloxanes.

6. A polymer precursor composition of Claim 1 wherein said
30 cationic photoinitiator is an onium salt of Group V, VI, and VII elements.

7. The polymer precursor composition of Claim 4 wherein the vinyl ether compounds comprise oligomers having the formula



where R' and R'' are H or an alkyl group having 1

5

to 10 carbon atoms

A is a moiety derived from at least one of the group consisting of urethanes, phenols, polyesters, polyethers, polysiloxanes, and polycarbonates, and has a molecular weight of about 400 to 10,000

10

Z is a moiety derived from a saturated

aliphatic or cyclo aliphatic

hydrocarbon or a polyalkylene ether

and has a molecular weight of about 28

to 250

15

n is an integer from 2 to 6

8. The polymer precursor composition of Claim 4 wherein the vinyl ether compounds comprise monomers having the formula



where R' and R'' are H or an alkyl group

20

having 1 to 10 carbon atoms

Z is a moiety derived from a saturated aliphatic or cyclo

aliphatic hydrocarbon or a poly alkylene ether

and has a molecular weight of about 28 to 250

n is an integer from 1 to 4

25

B is derived from at least one of the group

consisting of aliphatic and aromatic hydrocarbons,

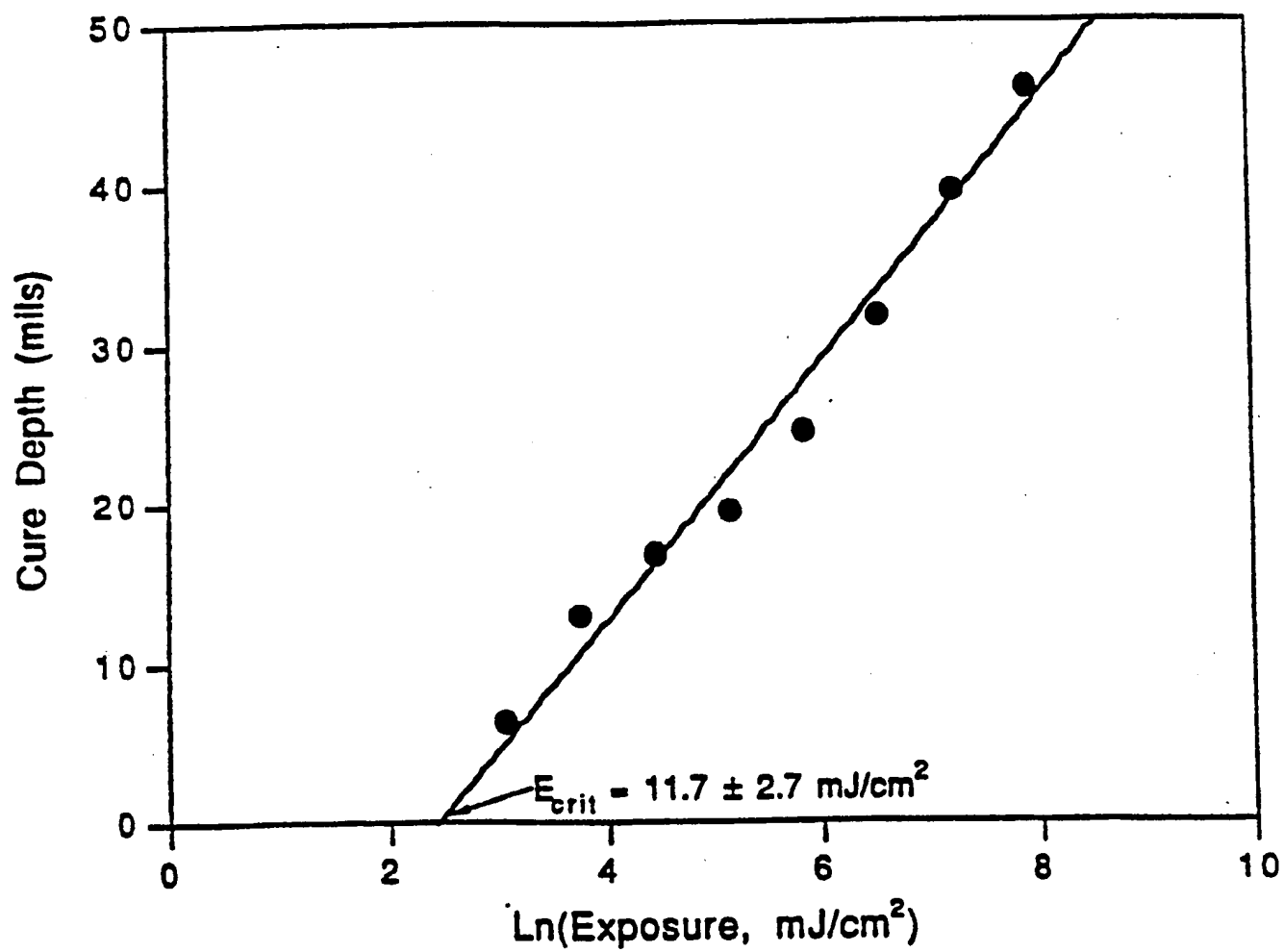
esters, ethers, siloxanes, urethanes, and carbonates,

and has a molecular weight of about 60 to 400.

9. In the process for forming a three-dimensional object from a liquid polymer precursor comprising repeatedly exposing the surface of a bath of said precursor to a beam of actinic light to solidify successive layers of said precursor the improvement comprising employing as said
- 5 fluid polymer precursor the composition of Claim 1.

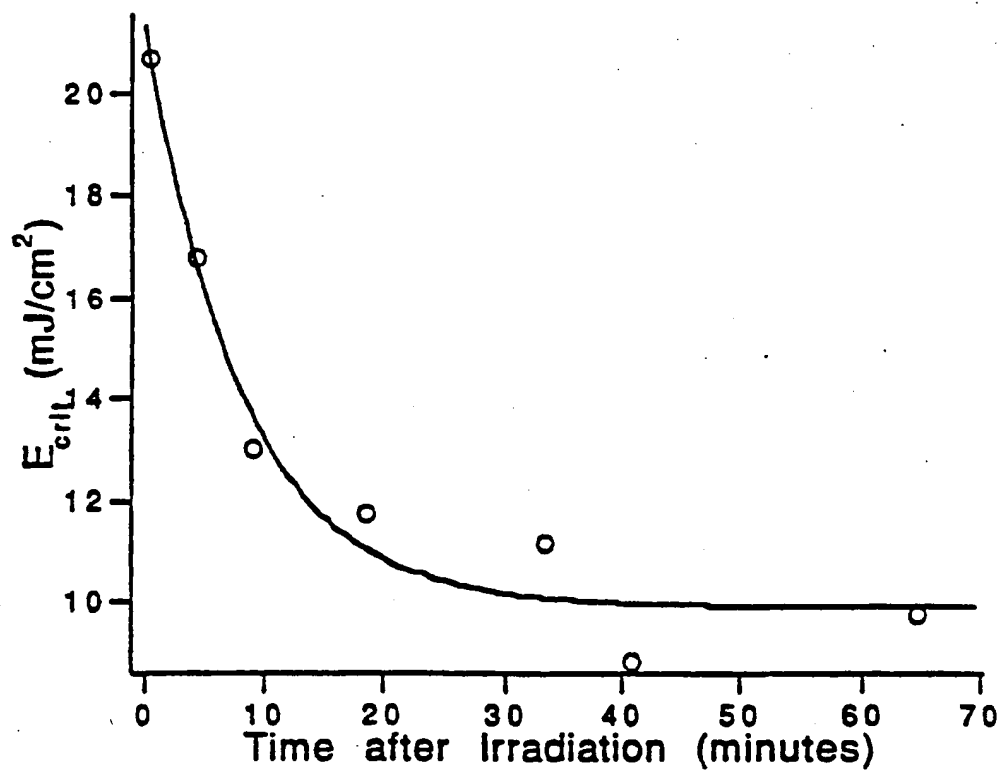
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Figure 1



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Figure 2



III. DOCUMENTS CONSIDERED TO BE RELEVANT

(CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
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ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9203168
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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